3-29-00

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JC780 U.S. PTO 03/28/00

PATENT

Attorney's Docket No.: U 012697-9

jc511 U.S. PTO 09/537252 03/28/00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of Inventors:

1. JOSE **JAMES**
2. RAJAN **JOSES**
3. ASHA MARY **JOHN**
4. JACOB **KOSHY**

WARNING: *The Declaration must name all of the actual inventor(s).*

For (title):

SINGLE STEP PROCESS FOR THE SYNTHESIS OF NANOPARTICLES OF CERAMIC OXIDE POWDERS

1. Type of Application

This new application is for a(n) (check one applicable item below):

☑ Original (nonprovisional)

☐ Design

☐ Plant

WARNING: ***Do not*** *use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4) unless the International Application is being filed as a divisional, continuation or continuation-in-part application.*

CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that this New Application Transmittal and the documents referred to as enclosed therein are being deposited with the United States Postal Service on this date **MARCH 28, 2000 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EL386268165US addressed to the: Assistant Commissioner of Patents, Washington, D.C. 20231**

JENNIFER RASHKIN
(type or print name of person mailing paper)

Jennifer Rash

(Signature of person mailing paper)

NOTE: ***Each paper or fee referred to as enclosed herein has the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 CFR 1.10(b).***

WARNING: ***Certificate of mailing (first class) or facsimile transmission procedures of 37 CFR 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.***

EL386268165US

WARNING: ***Do not*** *use this transmittal for the filing of a provisional application.*

2. Benefit of Prior U.S. Application(s) (35 U.S.C. 119(e), 120, or 121)

NOTE: If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

WARNING: *When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional* ***must*** *be filed prior to the Saturday, Sunday or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).*

☐ The new application being transmitted claims the benefit of prior U.S. application(s) and enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

NOTE: If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

☐ Divisional.

☐ Continuation.

☐ Continuation-in-Part (C-I-P).

3. Papers Enclosed That Are Required For Filing Date Under 37 CFR 1.53 (Regular) or 37 CFR 1.153 (Design) Application

__12__ Pages of specification

__2__ Pages of claims

__1__ Pages of Abstract

__15__ Sheets of drawing

- ☑ formal
- ☐ informal

WARNING: ***DO NOT*** *submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. Comments on proposed new 37 CFR 1.84. Notice of March 9, 1988 (1990 O.G. 57-62).*

NOTE: "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page." 37 C.F.R. 1.84(c).

(complete the following, if applicable)

☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)". 37 C.F.R. 1.84(b).

4. Additional papers enclosed

☐ Preliminary Amendment

☐ Information Disclosure Statement (37 CFR 1.98)

☐ Form PTO-1449

☐ Citations

☐ Declaration of Biological Deposit

☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.

☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative

☐ Special Comments

☐ Other

5. Declaration or oath

☐ Enclosed

executed by *(check **all** applicable boxes)*

☐ inventors.

☐ legal representative of inventors. 37 CFR 1.42 or 1.43

☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.

☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. *See item 13 below for fee.*

☑ Not Enclosed.

WARNING: *Where the filing is a completion in the U.S. of an International Application but where a declaration is not available or where the completion of the U.S. application contains subject matter in addition to the International Application the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.*

☑ Application is made by a person authorized under 37 CFR 1.41(c) on behalf of *all the above named inventors.* (The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently).

NOTE: *It is important that all the correct inventor(s) are named for filing under 37 CFR 1.41(c) and 1.53(b).*

☐ Showing that the filing is authorized. *(Not required unless called into question. 37 CFR 1.41(d).)*

6. Inventorship Statement

WARNING: *If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.*

The inventorship for all the claims in this application are:

☐ The same

☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

7. **Language**

NOTE: *An application including a signed oath or declaration may be filed in a language other than English. A verified English translation of the non-English language application and the processing fee of $130.00 required by 37 CFR 1.17(k) is required to be filed with the application or within such time as may be set by the Office. 37 CFR 1.52(d).*

NOTE: *A non-English oath or declaration in the form provided or approved by the PTO need not be translated. 37 CFR 1.69(b).*

☑ English

☐ non-English

☐ the attached translation is a verified translation. 37 CFR 1.52(d).

8. **Assignment**

☑ An assignment of the invention to COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

☑ will follow.

NOTE: *"If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).*

WARNING: *A newly executed "CERTIFICATE UNDER 37 CFR 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993. 1150 O.G. 62-64.*

9. **Certified Copy**

Certified copy of application

Country	Appln. No.	Filed

from which priority is claimed

☐ is attached.

☐ will follow.

NOTE: *The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 CFR 1.55(a) and 1.63.*

NOTE: *This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.*

10. **Fee Calculation (37 CFR 1.16)**

A. ☑ Regular Application

Claims as Filed

	Number Filed			Number Extra		Rate	Basic Fee 37 CFR 1.16(a) $690.00
Total Claims (37 CFR 1.16(c))	12	- 20	=	0	x	$ 18.00	
Independent Claims (37 CFR 1.16(b))	1	- 3	=	0	x	$ 78.00	
Multiple dependent claim(s), if any (37 CFR 1.16(d))					+	$ 260.00	

☐ Amendment cancelling extra claims enclosed.

☐ Amendment deleting multiple-dependencies enclosed.

☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 CFR 1.16(d).

Filing Fee Calculation $

B. ☐ Design application
($310.00 — 37 CFR 1.16(f))

Filing Fee Calculation $

C. ☐ Plant application
($480.00 — 37 CFR 1.16(g))

Filing Fee Calculation $

11. Small Entity Statement(s)

☐ Verified Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is(are) attached or has been filed.

Filing Fee Calculation (50% of **A**, **B** or **C** above) $

NOTE: Any excess of the full fee paid will be refunded if a verified statement and a refund request are filed within 2 months of the date of timely payment of a full fee. 37 CFR 1.28(a).

12. Request for International-Type Search (37 CFR 1.104(d)) ***(Complete, if applicable)***

☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

13. Fee Payment Being Made At This Time

☑ Not Enclosed

☑ No filing fee is to be paid at this time. *(This and the surcharge required by 37 CFR 1.16(e) can be paid subsequently.)*

☐ Enclosed

☐ basic filing fee $

☐ Recording assignment
($40.00; 37 CFR 1.21(h)) (See attached "COVER SHEET FOR ASSIGNMENT ACCOMPANYING NEW APPLICATION.")

☐ Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached.
($130.00; 37 CFR 1.47 and 1.17(h)) $

☐ For processing an application with a specification in a non-English language.
($130.00; 37 CFR 1.52(d) and 1.17(k)) $

☐ Processing and retention fee
($130.00; 37 CFR 1.53(d) and 1.21(l))

☐ Fee for international-type search report
($40.00; 37 CFR 1.21(e)). $

NOTE: 37 CFR 1.21(l) establishes a fee for processing and retaining any application which is abandoned for failing to complete the application pursuant to 37 CFR 1.53(d) and this, as well as the changes to 37 CFR 1.53 and 1.78, indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid or the processing and retention fee of §1.21(l) must be paid within 1 year from notification under §53(d).

Total fees enclosed $

14. Method of Payment of Fees

☐ Check in the amount of $

☐ Charge Account No. 12-0425 in the amount of $

A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).

15. Authorization to Charge Additional Fees

WARNING: *If no fees are to be paid on filing, the following items should not be completed.*

WARNING: *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.*

☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 12-0425.

☐ 37 CFR 1.16(a), (f) or (g) (filing fees)

☐ 37 CFR 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

☐ 37 CFR 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)

☐ 37 CFR 1.17 (application processing fees)

WARNING: *While 37 CFR 1.17(a), (b), (c) and (d) deal with extensions of time under §1.136(a), this authorization should be made only with the knowledge that: "Submission of the appropriate extension fee under 37 C.F.R. 1.136(a) is to no avail unless a request or petition for extension is filed." (Emphasis added). Notice of November 5,1985 (1060 O.G. 27)*

☐ 37 CFR 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 CFR 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b).

NOTE: 37 CFR 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application ... prior to paying, or at the time of paying, ... issue fee". From the wording of 37 CFR 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

16. Instructions As To Overpayment

☐ credit Account No. 12-0425

☐ refund

Signature of Attorney

Reg. No. 25,858

Tel. No. (212) 708-1945

William R. Evans
Ladas & Parry
26 West 61 Street
New York, NY 10023

☐ **Incorporation by reference of added pages**

(Check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)

☐ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added ___

☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added ___

☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added ___

☑ **Statement Where No Further Pages Added**

(If no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item:)

☑ This transmittal ends with this page.

SINGLE STEP PROCESS FOR THE SYNTHESIS OF NANOPARTICLES OF CERAMIC OXIDE POWDERS

Field of the invention

The present invention relates to a single step process for the synthesis of nanoparticles of ceramic oxide powders. More particularly, the present invention relates to a single step process for the synthesis of ceramic oxide powders using aqueous and non-aqueous precursors.

Background of the invention

Synthesis of nanoparticle ceramic powder is one of the major challenges for the development of advanced ceramics and specialty materials. The most important requirements for the powders of these materials are the availability of uniform nano-sized particles of well defined characteristics without agglomeration and controlled surface properties. Therefore, in recent years the processing of ultrafine, nanoparticles has gained tremendous importance [Chirino A.M. and Sproule R.T., American Ceramic Society Bulletin, Vol.59 (1980), pp.604; Gleiter, Nanostructured Materials, Vol.1 (1992), pp. 1; R.A. Andrievski, Journal of Materials Science, Vol.29 (1994), pp.614]. Nano sized particles, because of their high surface energy and driving force can be densified at much lower temperatures (by several hundreds of degrees) as compared to the large grained powders [W. H. Rhodes, Journal of American Ceramic Society, Vol.64 (1981), pp.19; J. R. Groza and R. J. Downing, Nanostructured Materials, Vol.7 (1981), pp. 749]. The final product will thus preserve the initial grain size of the powder and exhibit unique mechanical, optical, magnetic and electrical properties [M. S. Haji Mahmmod and L. S. Chumbley, Nanostructured Materials, Vol.7 (1996), pp.95; S. W. Mahon, R. F. Cochrane and M. A. Howson, Nanostructured Materials, Vol. 7 (1996), pp.195; C. Suryanarayana, Bulletin of Material Science, Vol.17 (1994), pp.307].

For the synthesis of oxide ceramic materials, chemical methods such as co-precipitation [R. Y. Bratto, American Ceramic Society Bulletin, Vol.48 (1969), pp.739], sol-

gel technique [G. I. Missing and M. Kumagai, Journal of American Ceramic Society, Vol. 72 (1989), pp.40] spray drying [J. G. Delau, American Ceramic Society Bulletin, Vol.49 (1970), pp.572] and freeze drying [Z. N. Nakagawa et al., Yogyo Kyokuishi 90 (1970) 313] are employed. In the case of co-precipitation methods it is very difficult to obtain homogeneous powders because in multi-component systems, various components precipitate at different pH values. In addition, the precipitate obtained needs calcination at elevated temperatures for getting useful powders. Sol-gel is a multiple step operation which involves calcination for prolonged duration at high temperatures for obtaining powders and processing of high volume off liquids with relatively low yield.

Recently, another processing technique, termed as self-sustained combustion or combustion synthesis, has been used to synthesis fine ceramic powders. This process of combustion synthesis involves rapid decomposition of a saturated aqueous solution, containing metal salts [J.J. Kingsley et al., J. Mater. Sci. 25 (1990) 1305; A. Pathak et al. Nanostructured Materials 8 (1997) 101; S.K. Saha et al. Nanostructured Materials 8 (1997) 29; Raveendranathan and Patil, K.C., J. Am. Ceram. Soc. Bull. 66 (1987) 688]. In the urea-nitrate method proposed by Patil et al the metal nitrate salts and urea are dissolved in minimum quantity of water and the solution was evaporated and burnt. For obtaining the required powder it was necessary to introduce the above solution to a preheated furnace (~500°C). In the hydrazine complex precursor route [Raveendranathan and Patil, K.C., J. Am. Ceram. Soc. Bull. 66 (1987) 688], the crystalline precursor complex is prepared from a solution containing metal salts and the appropriate hydrazine derivative salt. The cleaned precursor crystals thus obtained are burnt in air to get the required oxide powders. The above procedure is complex and involves less common reagents. The experimental procedure is also reported to be hazardous if not properly handled or controlled [K.C. Patil, Bull. Mater. Sci. 16 (1993) 588]. In another method for the preparation of fine oxide powders Pramanik et al.[S.K. Saha et al. Nanostructured Materials 8 (1997) 29] have used a solution containing

metal nitrates, urea (or Tri Ethyl Ammonium Carbonate) and Poly Vinyl Alcohol. In this method, to get phase pure powder of the material, it was essential to calcine the precursor at high temperatures (~900oC) for prolonged duration. Al these methods of self sustained combustion are limited to preparation of those compounds which have water soluble (aqueous) metal salts. Ceramic compounds having metals whose salts are mostly water insoluble (non-aqueous), like silicon containing compounds, cannot be prepared using the above reported methods.

Objects of the invention

The main object of the invention is to develop a process for the synthesis of nanoparticle ceramic oxide powders using metal salts that are even insoluble in water.

Another object of the invention is to provide a versatile process for the synthesis of nanoparticle ceramic oxide powders.

Another object of the invention is to synthesise compounds that are single component, two component or even multi-component systems.

Yet another object of the invention is to use a solvent which dissolves all the metal salts required for the preparation of a particular ceramic oxide.

Yet another object of the invention is to provide a process for the syntehsis of nanoparticle ceramic oxide powders without requiring the step of calcination.

It is a further object of the invention to provide a process for the synthesis of nanoparticle ceramic oxide powders without the step of calcination to obtain phase pure ultrafine powder is obtained at relatively low temperatures (~300°C) using a sand bath/hot plate.

Yet another object of the invention is to obtain any desired single phase ceramic oxide including complex systems in nanoparticulate form.

Another object of the invention is to provide a process for the synthesis of nanoparticle ceramic oxide powders that obviates the disadvantages associated with the prior art processes.

Summary of the invention

Accordingly, the present invention relates to a single step process for the synthesis of nanoparticles of phase pure ceramic oxides of a single or a multi-component system comprising one or more metal ions, said process comprising,

(a) preparing a solution containing all the required metal ions in stoichiometric ratio by dissolving their respective soluble salts in an organic solvent or in water,

(b) preparing a precursor by complexing the metal ions with a complexing agent while keeping the ratio of the charges of the acid to the charges of the metal ions as unity;

(c) adjusting the nitrate/ammonia content in the system;

(d) heating the system from room temperature to 250-300°C.

In one embodiment of the invention, the desired oxide contains (a) one cation selected from the group comprising of Al_2O_3, ZrO_2, TiO_2, CeO_2, HfO_2, MgO, SiO_2, (b) two cations of the general formula ABO_3, wherein A is Si, Al, Y or Lanthanides, B is Ba, Sr, Ca, Mg or Fe; with general formula AlM_2O_5, where M = Ti, Zr or Hf; or with general formula Al_2NO_4, where N = Mg, Ca, Sr, Ba, Zn, (c) three cations with the general formula $A(B_{0.5}B'_{0.5})O_6$ or $A_2(BB')O_6$, where A is Ba, Sr, Ca or Mg, B is Zr, Hf, Sb or Sn, B' is Al, Y or Lanthanides, (d) four cations with general formula $(AA')(BB')O_6$, where A and A' are Ba, Sr, Ca or Mg, B is Zr, Hf, Sb or Sn, B' is Al, Y or Lanthanides.

In another embodiment of the invention, the complexing agent is selected from the group comprising of citric acid, EDTA and oxalic acid.

In another embodiment of the invention, the nitrate/ammonia content in the system is adjusted by addition of ammonium nitrate where the precursor is formed in an organic solvent.

In yet another embodiment of the invention, the nitrate/ammonia content in the system is adjusted by the addition of nitric acid and ammonia or ammonium nitrate where the precursor complex is formed in water.

In another embodiment of the invention, water insoluble metal salts are brought into solution by dissolving them in an organic solvent.

In another embodiment of the invention, the metal salts are selected from the group comprising of alkoxides, nitrates, chlorides, sulphates, oxychlorides or any other salts that are soluble in an organic solvent.

In a further embodiment of the invention, the water insoluble oxides and carbonates of the desired metal are dissolved in suitable acids prior to use.

In yet another embodiment of the invention, any metal that can be dissolved to form a solution can be used for making their oxides.

In yet another embodiment of the invention, the organic solvent is selected from the group comprising of alcohols, trichloroethylene, and any other solvent capable of dissolving the complexing agent and any one of the metal salts needed to form the desired oxide.

In a further embodiment of the invention, the organic solvent is selected from the group comprising of ethyl alcohol, methyl alcohol and isopropyl alcohol.

In yet another embodiment of the invention, the combustion is self-ignited and propagated when heated.

In a further embodiment of the invention, the heating is done on a sand bath/hot plate.

Brief description of the accompanying drawings

Figure 1(a) gives the X-ray diffraction patterns of the precursor of the ceramic oxides prepared by the process of the present invention confirming that the powder obtained is pure SiO_2.

Figure 1(b) gives the FT-IR spectrum of the precursors confirming that combustion is complete and that no organic matter is present in the system.

Figure 2(a) gives the X-ray diffraction patterns of precursor powders (both Alumina I and Alumina II) heated at 900°C for 2 hours showing that the alumina is still amorphous.

Figure 2 (b) gives the X-ray diffraction patterns of both precursor powders Alumina I and Alumina II heated at 1100°C for 4 hours confirming that the powder is phase pure.

Figure 2 (c) is the FT-IR spectrum of both precursor powders Alumina I and Alumina II confirming that combustion is complete and that no organic matter is present in the system.

Figure 3 (a) gives the X-ray diffraction patterns of a precursor confirming that the powder obtained is phase pure $CaSiO_3$.

Figure 3 (b) gives the FT-IR spectrum corresponding to precursor of X-ray diffraction shown in figure 3(a) and shows that combustion is complete and that no organic material is present in the system.

Figure 4 (a) gives the X-ray diffraction pattern for the precursor powder $BaZrO_3$ confirming that the powder is phase pure.

Figure 4 (b) gives the corresponding FT-IR spectrum for $BaZrO_3$ showing that combustion is complete and that no organic matter is present in the system.

Figure 5 (a) is the X ray diffraction pattern for the precursor Aluminium Barium Zirconate showing that the powder obtained is phase pure.

Figure 5 (b) gives the FT-IR spectrum for the precursor Aluminium Barium Zirconate confirming that combustion is complete and that no organic matter is present in the system.

Figure 6 (a) gives the X-ray diffraction pattern for the precursor YBa_2ZrO_3 showing that the powder is phase pure.

Figure 6 (b) is the corresponding FT-IR spectrum for the precursor YBa_2ZrO_3 showing that combustion is complete and that no organic matter is present in the system.

Figure 7 (a) is the X-ray diffraction pattern for the precursor $LaBaSrZrO_{5.5}$ showing that the powder is phase pure.

Figure 7 (b) gives the FT-IR spectrum for the precursor $LaBaSrZrO_{5.5}$ confirming that combustion is complete and that no organic matter is present in the system.

Detailed description of the invention

The present invention provides a new one-step process for the synthesis of nanoparticulate oxide ceramics at low temperature using only a sand bath/hot plate. The details of the procedure for the synthesis of ultra fine ceramic oxide powder comprises of,

(1) Preparation of the solution of all the metal salts in the same solvent and mixing them in required ratios.

(2) Addition of required quantity of an organic complexing agent like Citric acid or Ethylin Diamine Tetra Acetic acid (EDTA) to the solution.

(3) Adjusting the nitrate/ammonia content in the system

(4) Heating the solution on a sand bath/hot plate

The salts of metals may be selected from its alkoxides, oxides, nitrates, oxychlorides, carbonates or anything, which could be dissolved in the same solvent. The ammonia/nitrate content is adjusted by addition of the appropriate reagents. Ammonia/nitrate could be added as $(NH_4)^+/NO_3$ or any of their derivatives depending on the system selected. The oxide powders obtained by this method are characterised by X-ray diffraction, FT-IR,TEM and particle size analysis.

The solvent used may be ethyl alcohol, methyl alcohol, isopropyl alcohol, trichloroethylene, water etc.

The details of the invention is described in the examples given below which are provided by way of illustration only and should not be construed to limit the scope of the invention.

Example 1

Synthesis of nanoparticles of SiO_2

Tetraethylorthosilicate (2 ml) and citric acid (3.343 g) were dissolved in ethyl alcohol (20 ml) in a glass beaker. To this solution sufficient quantity of ammonium nitrate was added to adjust the ammonia/nitrate content in the system. The beaker containing the solution was heated in a hot plate. Initially the solution boils and undergoes dehydration followed by decomposition leading to smooth deflation with enormous swelling, producing a foam. The foam then ignites and the product of combustion is voluminous and fluffy ultra fine powder of SiO_2.

The X-ray diffraction patterns of the precursor is given in figure (a) which confirms that the powder obtained is phase pure SiO_2. The FT-IR spectrum shown in figure 1(b) confirms that the combustion is complete and no organic matter is present in the system. The TEM examination of the powders give the particle sizes in the range of 50-400 m. The particle size analysis of the samples has shown that more than 505 of the particles/agglomerates have size less than 900 nm which corroborates the TEM results.

Example 2

Synthesis of ultrafine particles of Al_2O_3

Aluminium nitrate (10 g) and EDTA (5.84 g) were dissolved in 25 ml of water in separate glass beakers. They were then mixed together and the nitrate ammonia content were adjusted by the addition of nitric acid/ammonium hydroxide. The beaker containing the solution is heated in a sand bath. Initially the solution boils and undergoes dehydration followed by decomposition leading to smooth deflation with enormous swelling, producing a foam. The foam then ignites and propagates by itself and the product of combustion is voluminous and fluffy ultra fine powder of alumina (Alumina-I).

The same procedure as above was carried out with ethanol as solvent and adjusting the Nitrate/ammonia content using ammonium nitrate. The sample is labelled as Alumina-II.

The direct products after combustion was amorphous but crystallised into hexagonal structure at about 1100°C. The X-ray diffraction patterns of the precursor powders (both Alumina-I and Alumina-II) heated at 900°C for 2 hours has shown that alumina is still amorphous and those heated at 1100°C for 4 hours, shown in Figures 2(a&b) confirms that the powder obtained is phase pure. The FT-IR spectrum shown in figure 2(c) confirms that the combustion is complete and no organic matter is present in the system. The TEM examination of the powders give the particle sizes in the range of 50-400 nm. The particle size analysis of the samples has shown that more than 50% of the particles/agglomerates have size less than 800 nm which corroborates the TEM results.

Example 3

Synthesis of ultrafine particles of Calcium Silicates

Stoichiometric amounts of calcium nitrate (6.345 g) and Tetraethyl orthosilicate (3 ml) and citric acid (7.5292 g) were dissolved in ethyl alcohol (50 ml). To this solution sufficient quantity of ammonium nitrate was added to adjust the ammonia/nitrate content in the system. The beaker containing the solution was heated in a hot plate. Initially the solution boils and undergoes dehydration followed by decomposition leading to smooth deflation with enormous swelling, producing a foam. The foam then ignites and the product of combustion is voluminous and fluffy ultrafine powder of calcium silicates. Depending on the amount of calcium nitrate used we can get monocalcium silicate ($CaSiO_3$), dicalcium silicate (Ca_2SiO_4) or tricalcium silicate (Ca_3SiO_5).

The X-ray diffraction patterns of the precursor is given in figure 3(a) which confirms that the powder obtained is phase pure CaSiO3.The FT-IR spectrum shown in figure 3(b) confirms that the combustion is complete and no organic matter is present in the system. The TEM examination of the powders give the particle sizes in the range of 50-40 nm. The particle size analysis of the samples has shown that more than 50% of the particles/agglomerates have size less than 850 nm which corroborates the TEM results.

Example 4

Synthesis of nanoparticulate $BaZrO_3$

Analytical grade $Ba(NO_3)_2.5H_2O$ (1.233 g) and $ZrOCl_2.8H_2O$ (1 g) were dissolved in distilled water. They were then mixed in a glass beaker so as to get the desired stoichiometry. To this mixture, appropriate amount of citric acid (1.3047 g) was added and the nitrate/ammonia content was controlled by the addition of nitric acid and ammonium hydroxide. The beaker containing the solution is heated in a sand bath. Initially the solution boils and undergoes dehydration followed by decomposition leading to smooth deflation with enormous swelling, producing a foam. The foam then ignites and the product of combustion is voluminous and fluffy ultrafine powder of $BaZrO_3$.

The X-ray diffraction patterns of the precursor is given in figure 4(a) which confirms that the powder obtained is phase pure. The FT-IR spectrum shown in figure 4(b) confirms that the combustion is complete and no organic matter is present in the system. The TEM examination of the powders give the particle sizes in the range of 50-400 nm. The particle size analysis of the samples has shown that more than 55% of the particle/agglomerates have size less than 800 nm which corroborates the TEM results.

Example 5

Synthesis of ultrafine particles of $AlBa_2ZrO_{5.5}$

Stoichiometric amounts of $Al(NO_3)_3.9H_2O$, $ZrO(NO_3)2.8H_2O$ and citric acid were dissolved in ethyl alcohol and $Ba(NO_3)_2.5H_2O$ in water in a glass beaker. In typical experiment 11.641 g of $Al(NO_3)_3.9H_2O$, 10 g of $ZrO(NO_3)_2.8H_2O$ and 23.912 g of citric acid were dissolved in 25 ml of ethanol and 12.248 g of $Ba(NO_3)_2.5H_2O$ in water each in separate glass beakers. The nitrate/ammonia content in the solution was adjusted by the addition of ammonium nitrate. The stoichiometry of the redox mixture was calculated from the total valency of the oxidising and reducing agents. The beaker containing the solution was heated in a hot plate. Initially the solution boils and undergoes dehydration followed by

decomposition leading to smooth deflation with enormous swelling, producing a foam. The foam then ignites and the product of combustion is voluminous and fluffy ultrafine powder of aluminium Barium Zirconate.

The X-ray diffraction patterns of the precursor is given in figure 5(a) which confirms that the powder obtained is phase pure. The FT-IR spectrum shown in figure 5(b) confirms that the combustion is complete and no organic matter is present in the system. The TEM examination of the powders give the particle sizes in the range 50-400 nm. The particle size analysis of the samples has shown that more than 50% of the particles/agglomerates have size less than 800 nm which corroborates the TEM results.

Example 6

Synthesis of nanoparticulate $YBa_2ZrO_{5.5}$

Analytical grade Y_2O_3 (1.725 g) and $BaCO_3$ (6.127 g)were dissolved in nitric acid and $ZrOCl_2.8H_2O$ (5 g) in distilled water. They were then mixed in a glass beaker so as to get the desired stoichiometry. To this mixture appropriate amount of citric acid (10.935 g) was added and the nitrate/ammonium content was controlled by the addition of nitric acid and ammonium hydroxide. The beaker containing the solution is heated in a sand bath. Initially the solution boils and undergoes dehydration followed by decomposition leading to smooth deflation with enormous swelling, producing a foam. The foam then ignites and the product of combustion is voluminous and fluffy ultrafine powder of $YBa_2ZrO_{5.5}$.

The X-ray diffraction patterns of the precursor is given in figure 6(a) which confirms that the powder obtained is phase pure. The FT-IR spectrum shown in figure 6(b) confirms that the combustion is complete and no organic matter is present in the system. The TEM examination of the powder give the particle sizes in the range of 50-400 nm. The particle size analysis of the samples has shown that more than 55% of the particle/agglomerates have size less than 800 nm which corroborates the TEM results.

Example 7

Synthesis of ultrafine $LaBaSrZrO_{5.5}$

The starting materials were analytical grade La_2O_3 (2.528 g), $BaCO_3$ (1.711 g), $ZrCO_3$ (0.9062 g) and $ZrOCl_{2.8}H_2O$ (1.97 g). Because of the poor solubility of La_2O_3 and $BaCO_3$ and $SrCO_3$ in water, they were dissolved in nitric acid and $ZrOCl_{2.8}H_2O$ in water. To this an equivalent quantity of citric acid (4.729 g) was added and the ammonia/nitrate content was controlled by the addition of ammonium nitrate. The beaker containing the solution is heated in a hot plate. Initially the solution boils and undergoes dehydration followed by decomposition leading to smooth deflation with enormous swelling, producing a foam. The foam then ignites and the product of combustion is voluminous and fluffy ultrafine powder of $LaBaSrZrO_{5.5}$.

The X-ray diffraction patterns of the precursor is given in figure 8(a) which confirms that the powder obtained is phase pure. The FT-IR spectrum shown in figure 7(b) confirms that the combustion is complete and no organic matter is present in the system. The TEM examination of the powders give the particle sizes in the range of 50-400 nm. The particle size analysis of the samples has shown that about 50% of the particle/agglomerates have size less than 800 nm which corroborates the TEM results.

We claim

1. A single step process for the synthesis of nanoparticles of phase pure ceramic oxides of a single or a multi-component system comprising one or more metal ions, said process comprising,

(e) preparing a solution containing all the required metal ions in stoichiometric ratio by dissolving their respective soluble salts in an organic solvent or in water,

(f) preparing a precursor by complexing the metal ions with a complexing agent while keeping the ratio of the charges of the acid to the charges of the metal ions as unity;

(g) adjusting the nitrate/ammonia content in the system;

(h) heating the system from room temperature to 250-300°C.

2. A process as claimed in claim 1 wherein the desired oxide contains (a) one cation selected from the group comprising of Al_2O_3, ZrO_2, TiO_2, CeO_2, HfO_2, MgO, SiO_2, (b) two cations of the general formula ABO_3, wherein A is Si, Al, Y or Lanthanides, B is Ba, Sr, Ca, Mg or Fe; with general formula AlM_2O_5, where M = Ti, Zr or Hf; or with general formula Al_2NO_4, where N = Mg, Ca, Sr, Ba, Zn, (c) three cations with the general formula $A(B_{0.5}B'_{0.5})O_6$ or $A_2(BB')O_6$, where A is Ba, Sr, Ca or Mg, B is Zr, Hf, Sb or Sn, B' is Al, Y or Lanthanides, (d) four cations with general formula $(AA')(BB')O_6$, where A and A' are Ba, Sr, Ca or Mg, B is Zr, Hf, Sb or Sn, B' is Al, Y or Lanthanides.

3. A process as claimed in claim 1 wherein the complexing agent is selected from the group comprising of citric acid, EDTA and oxalic acid.

4. A process as claimed in claim 1 wherein the nitrate/ammonia content in the system is adjusted by addition of ammonium nitrate where the precursor is formed in an organic solvent.

5. A process as claimed in claim 1 wherein the nitrate/ammonia content in the system is adjusted by the addition of nitric acid and ammonia or ammonium nitrate where the precursor complex is formed in water.

6. A process as claimed in claim 1 wherein water insoluble metal salts are brought into solution by dissolving them in an organic solvent.

7. A process as claimed in claim 1 wherein the metal salts are selected from the group comprising of alkoxides, nitrates, chlorides, sulphates, oxychlorides or any other salts that are soluble in an organic solvent.

8. A process as claimed in claim 1 wherein the water insoluble oxides and carbonates of the desired metal are dissolved in suitable acids prior to use.

9. A process as claimed in claim 1 wherein the organic solvent is selected from the group comprising of alcohols, trichloroethylene, and any other solvent capable of dissolving the complexing agent and any one of the metal salts needed to form the desired oxide.

10. A process as claimed in claim 9 wherein the alcohol is selected from the group comprising of ethyl alcohol, methyl alcohol and isopropyl alcohol.

11. A process as claimed in claim 1 wherein the combustion is self-ignited and propagated when heated.

12. A process as claimed in claim 11 wherein the heating is done on a sand bath/hot plate.

ABSTRACT

The present invention relates to a single step process for the synthesis of nanoparticles of phase pure ceramic oxides of a single or a multi-component system comprising one or more metal ions. The process comprises preparing a solution containing all the required metal ions in stoichiometric ratio by dissolving their respective soluble salts in an organic solvent or in water, preparing a precursor, adjusting the nitrate/ammonia content in the system, and heating the system.

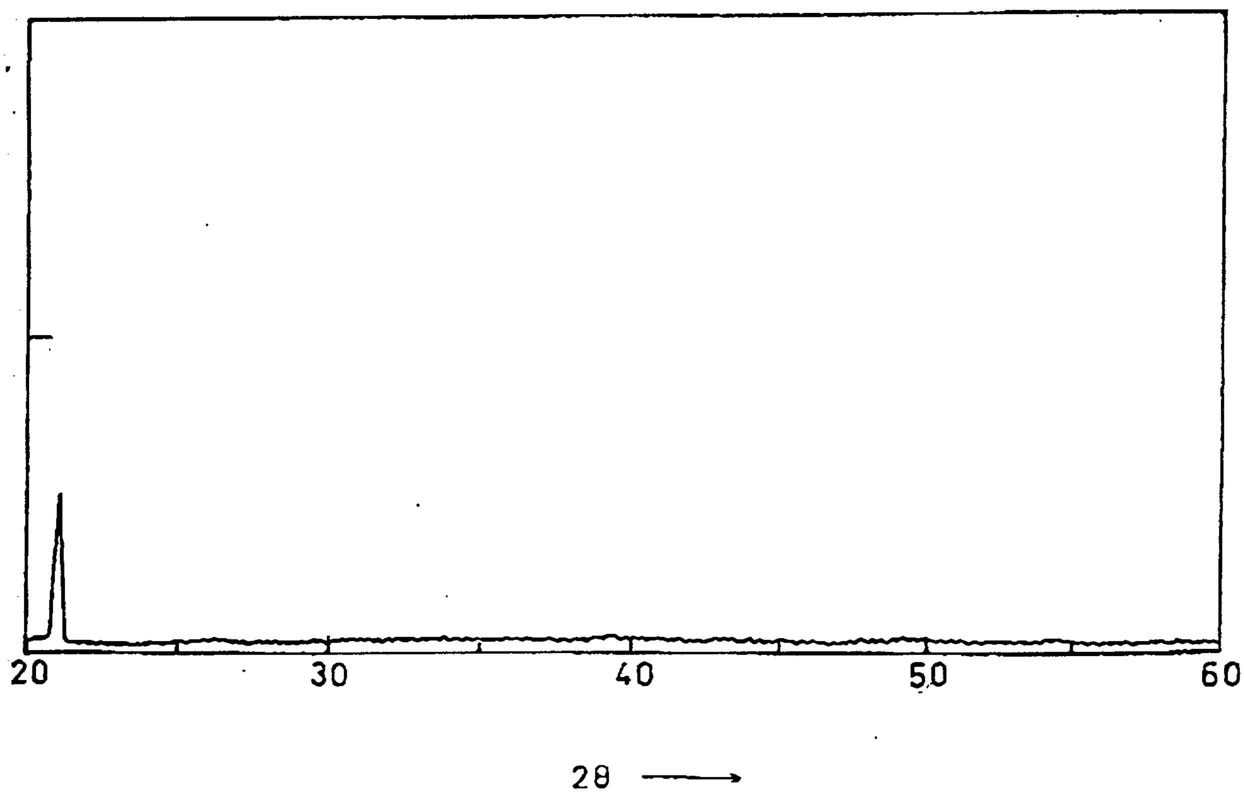


Fig 1(a)

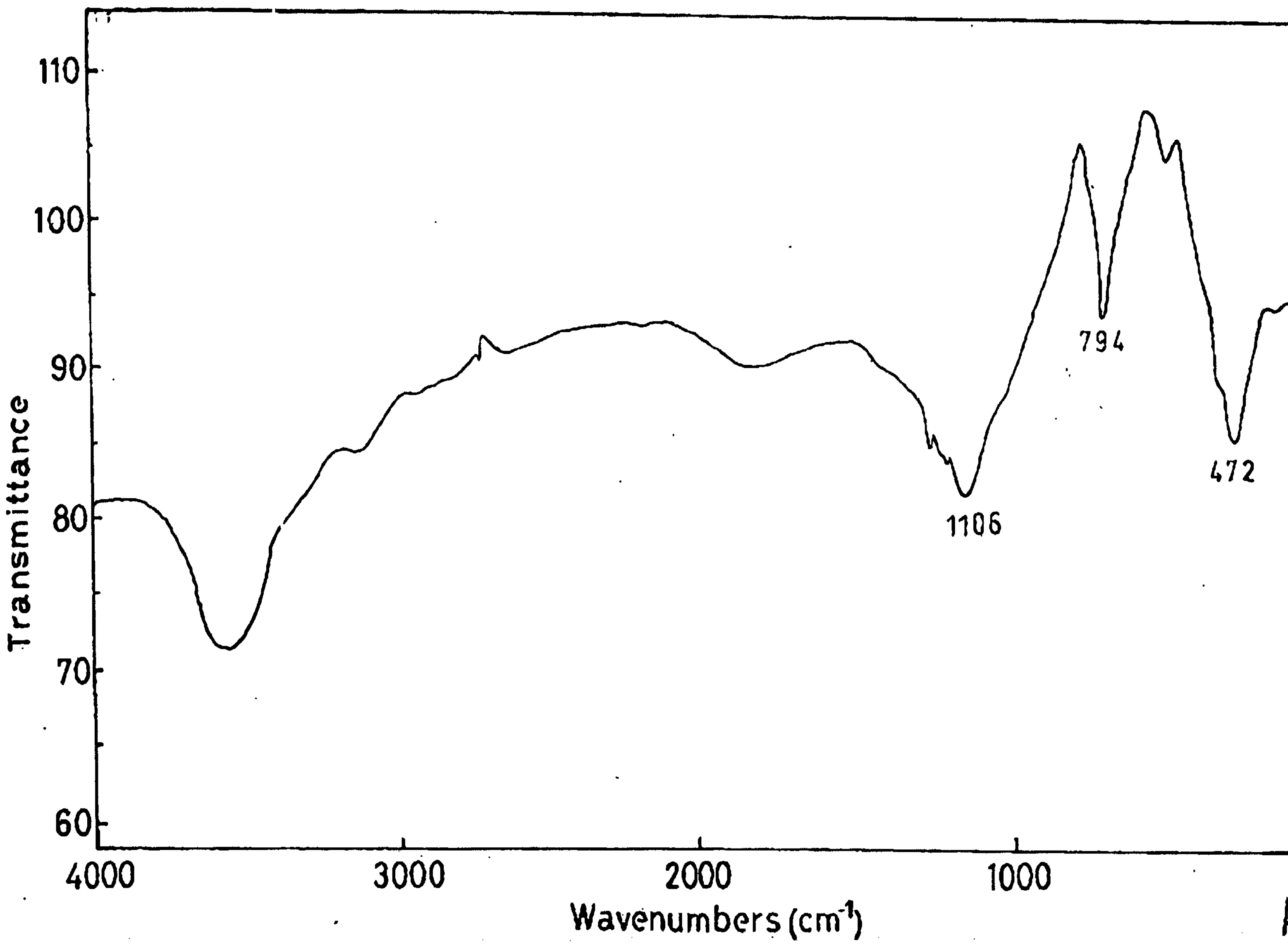

Transmittance
110
100
90
80
70
60
4000
3000
2000
1000
Wavenumbers (cm-1)
1106
794
472

Fig 1(b)

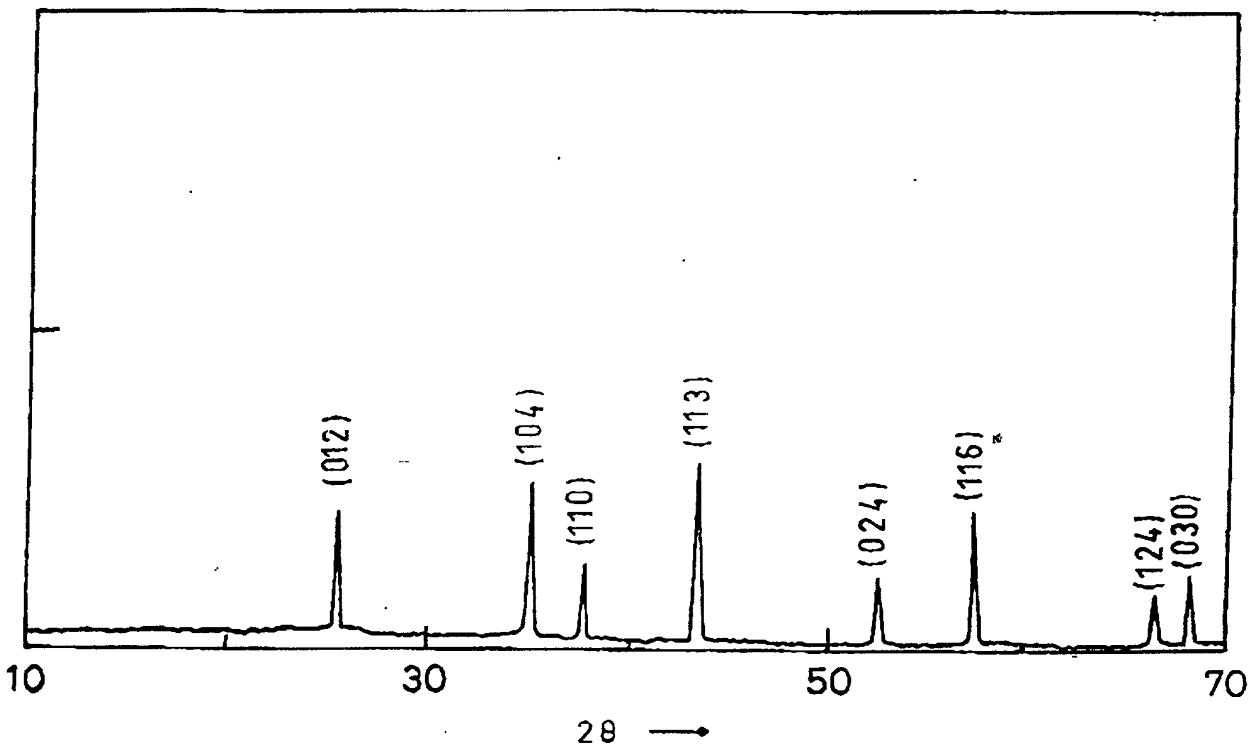


Fig 2(a)

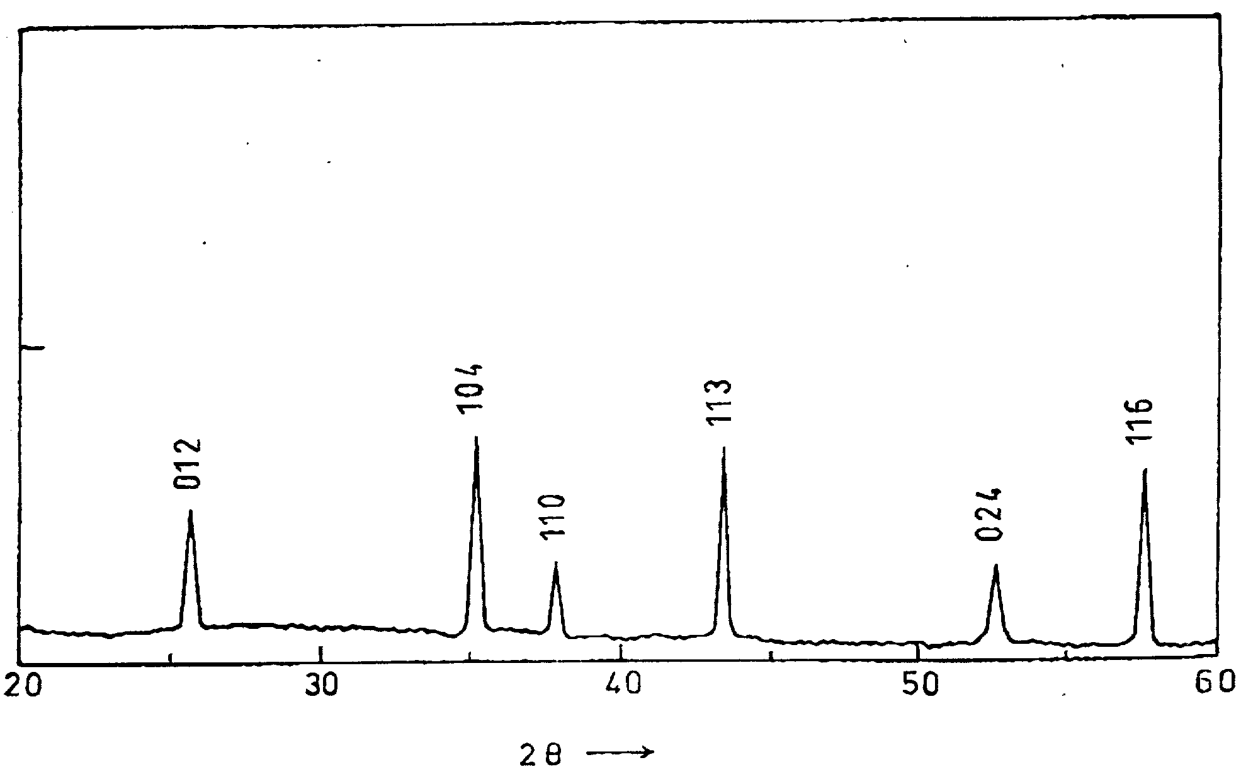
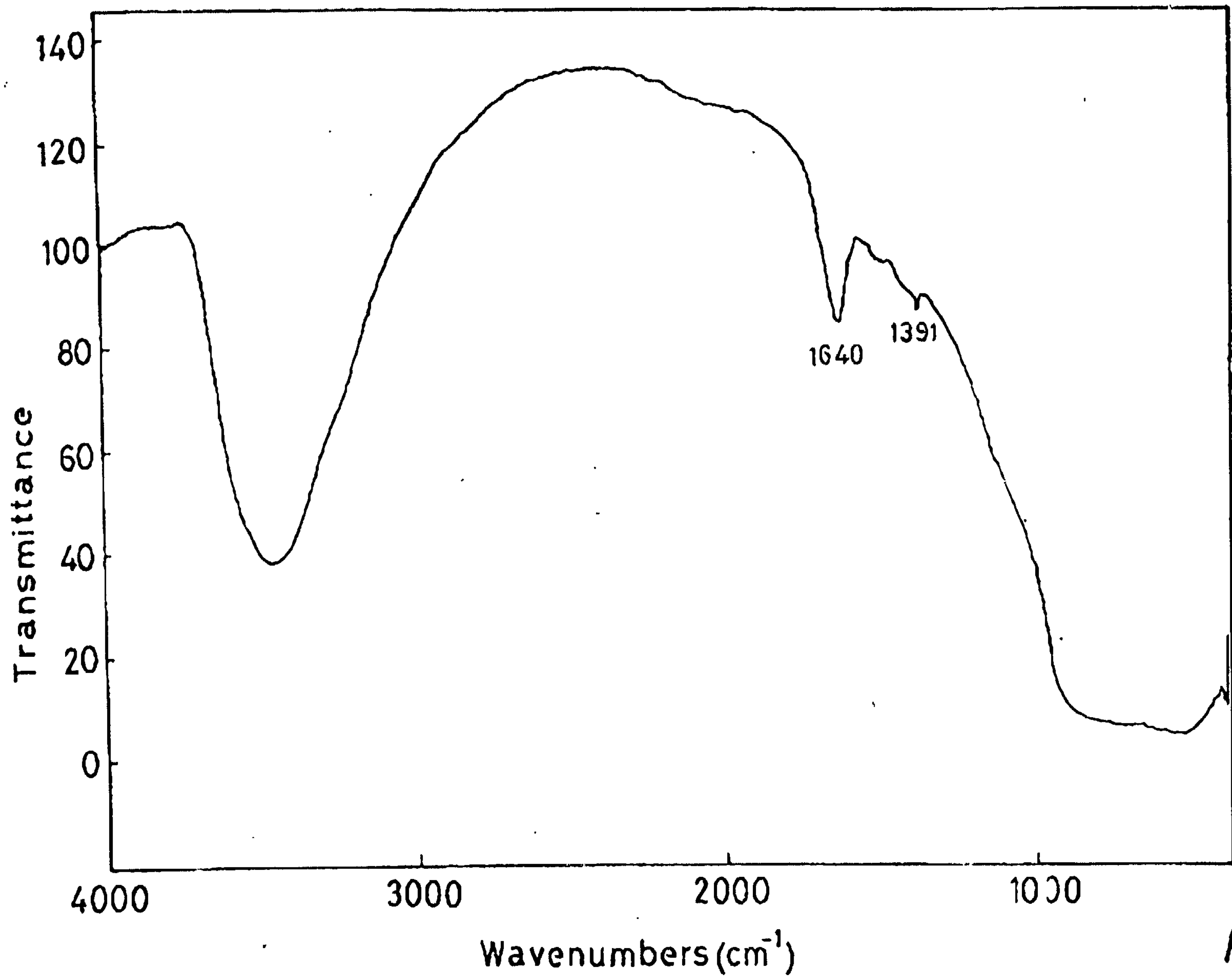


Fig 2(b)



Transmittance
140
120
100
80
60
40
20
0
1640
1391
4000
3000
2000
1000
Wavenumbers (cm⁻¹)

Fig 2(c)

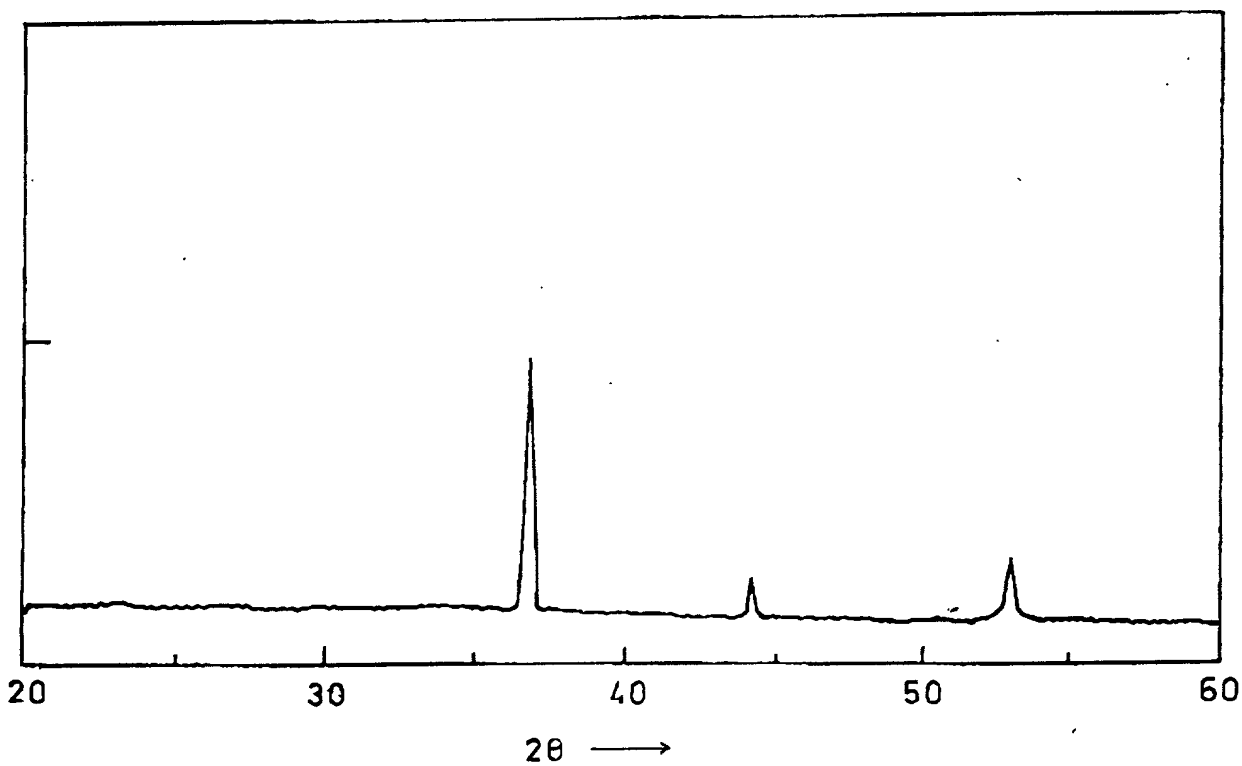
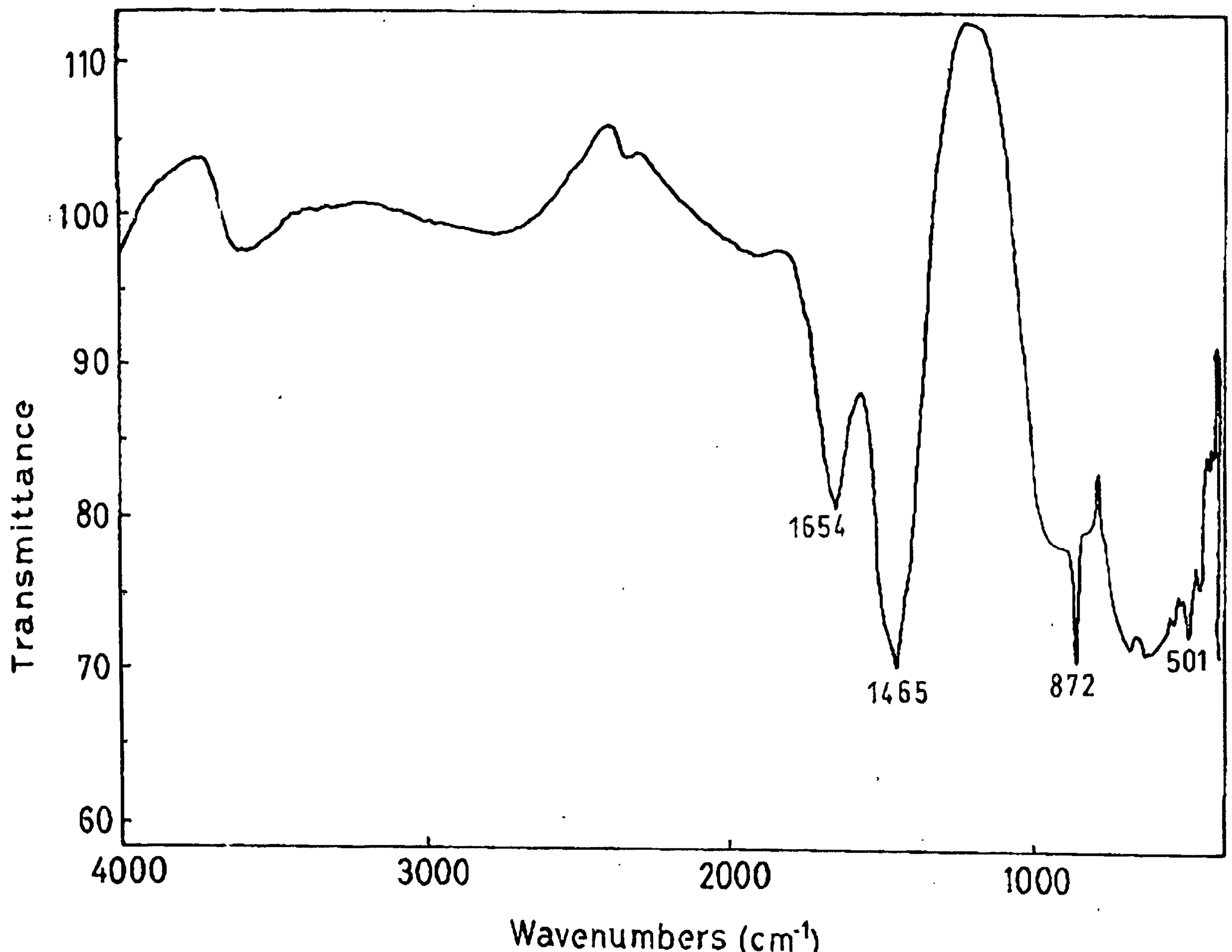


Fig 3(a)



Transmittance
110
100
90
80
70
60
1654
1465
872
501
4000
3000
2000
1000
Wavenumbers (cm⁻¹)

Fig 3(b)

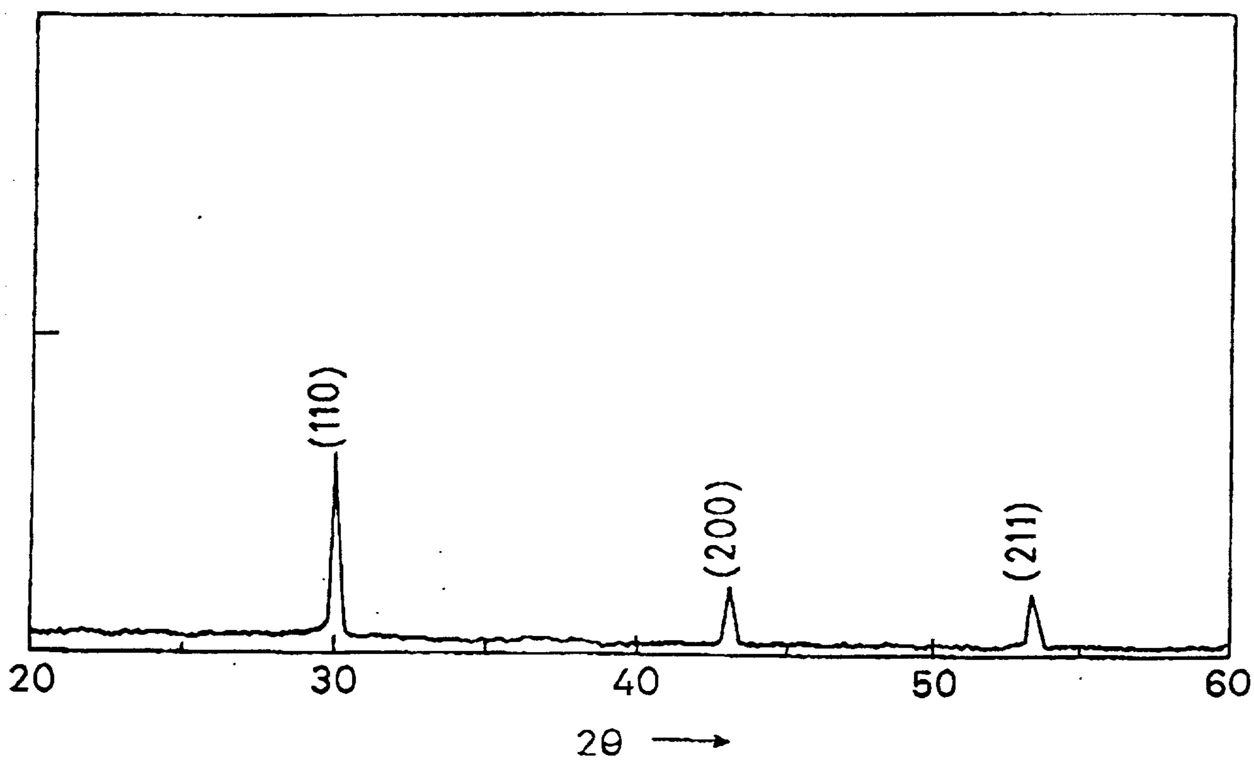
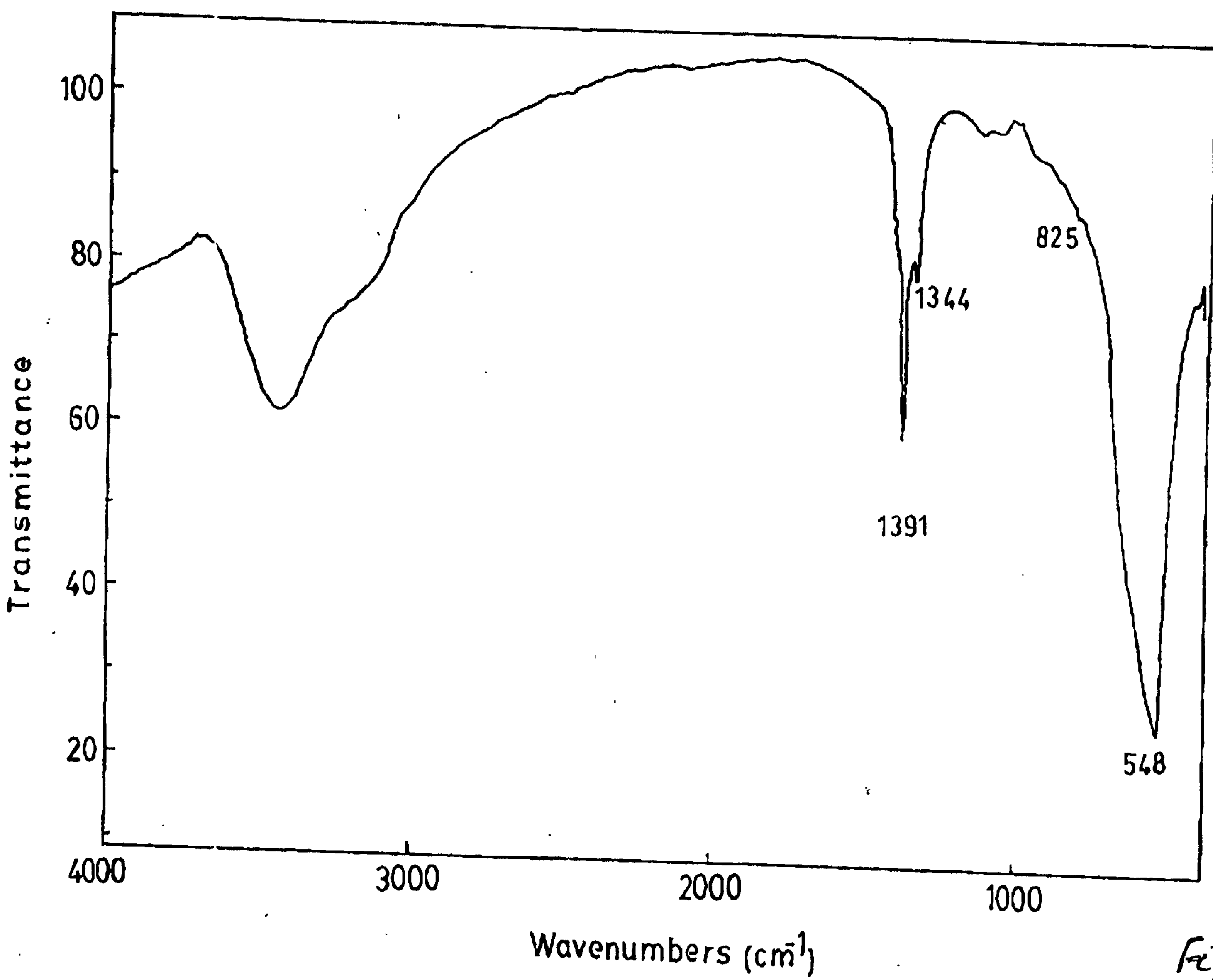


Fig 4(a)



Transmittance
100
80
60
40
20
4000
3000
2000
1000
Wavenumbers (cm^{-1})
1391
1344
825
548

Fig 4(b)

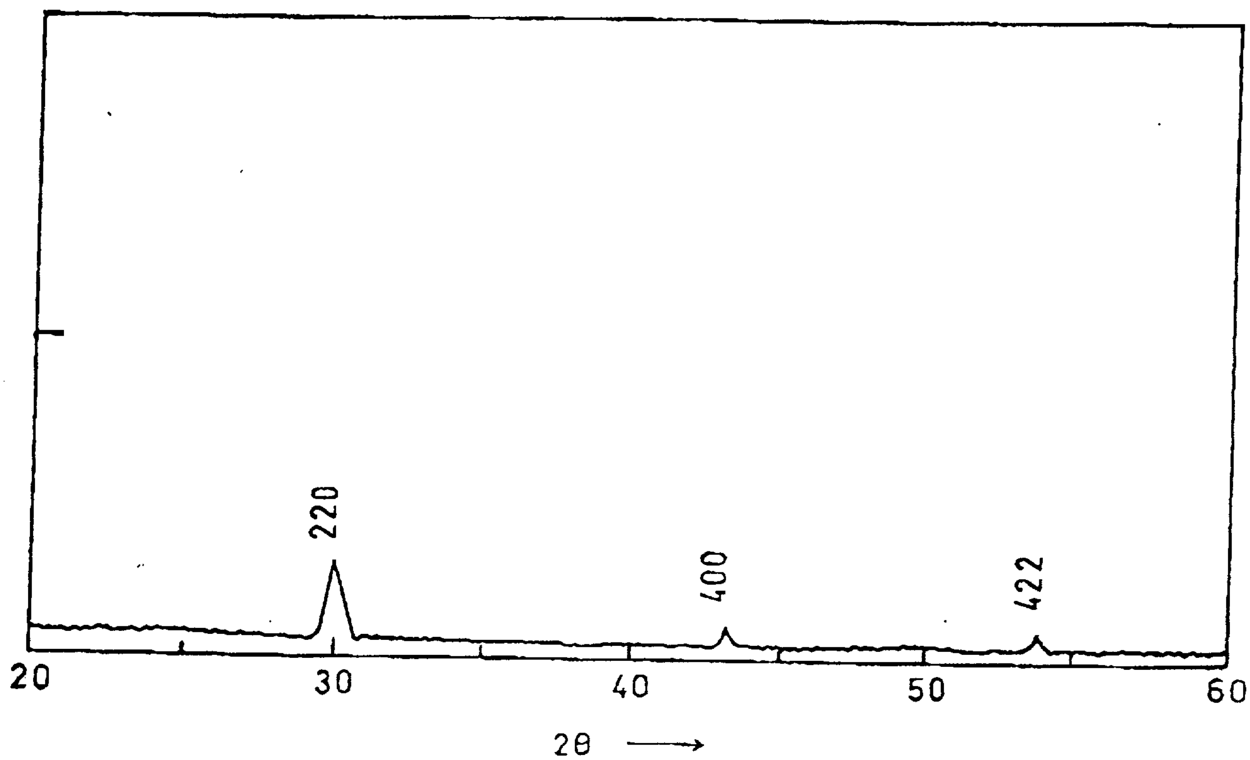
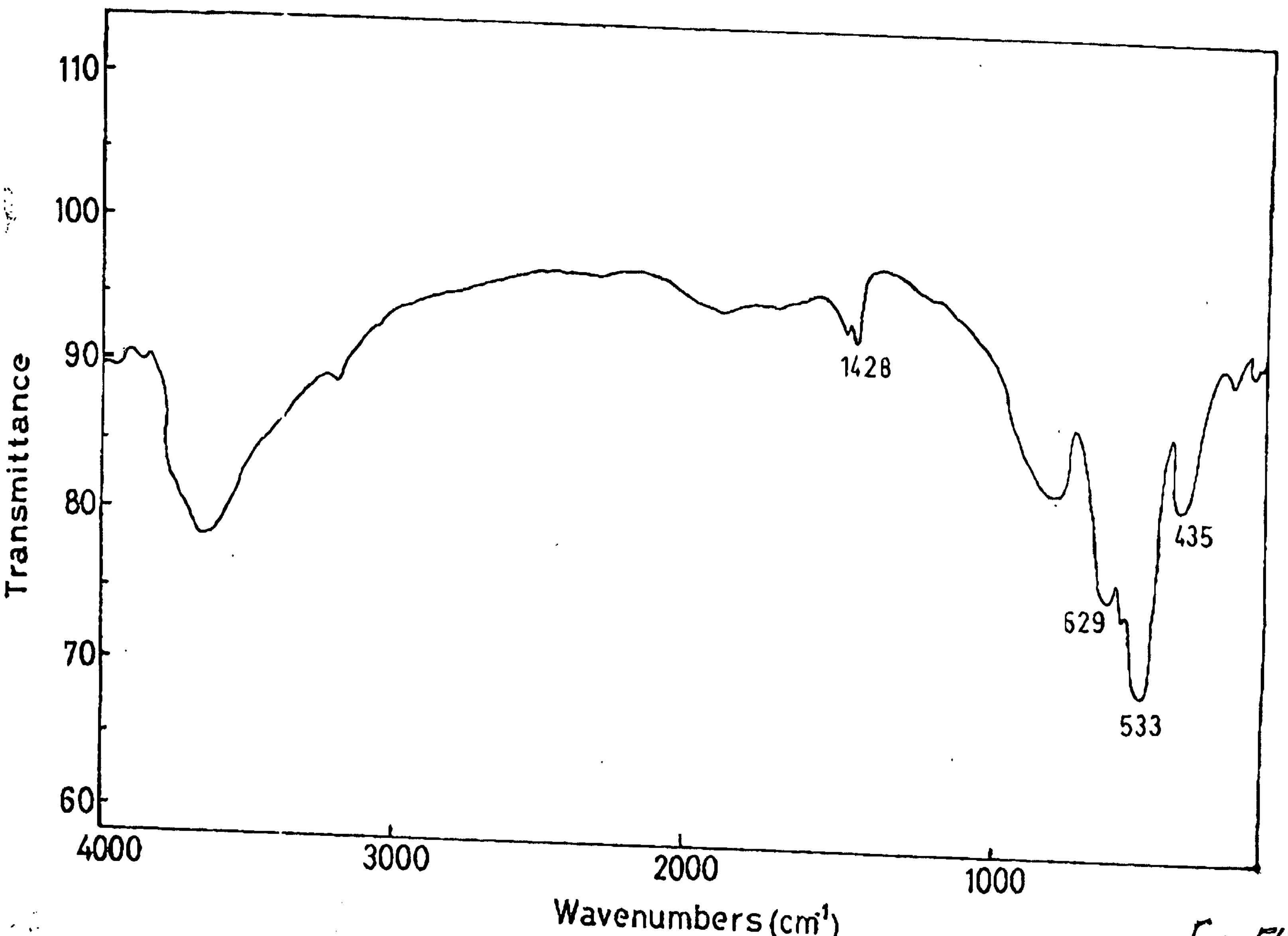


Fig 5(a)



Transmittance
110
100
90
80
70
60
4000
3000
2000
1000
Wavenumbers (cm⁻¹)
1428
629
533
435

Fig 5(b)

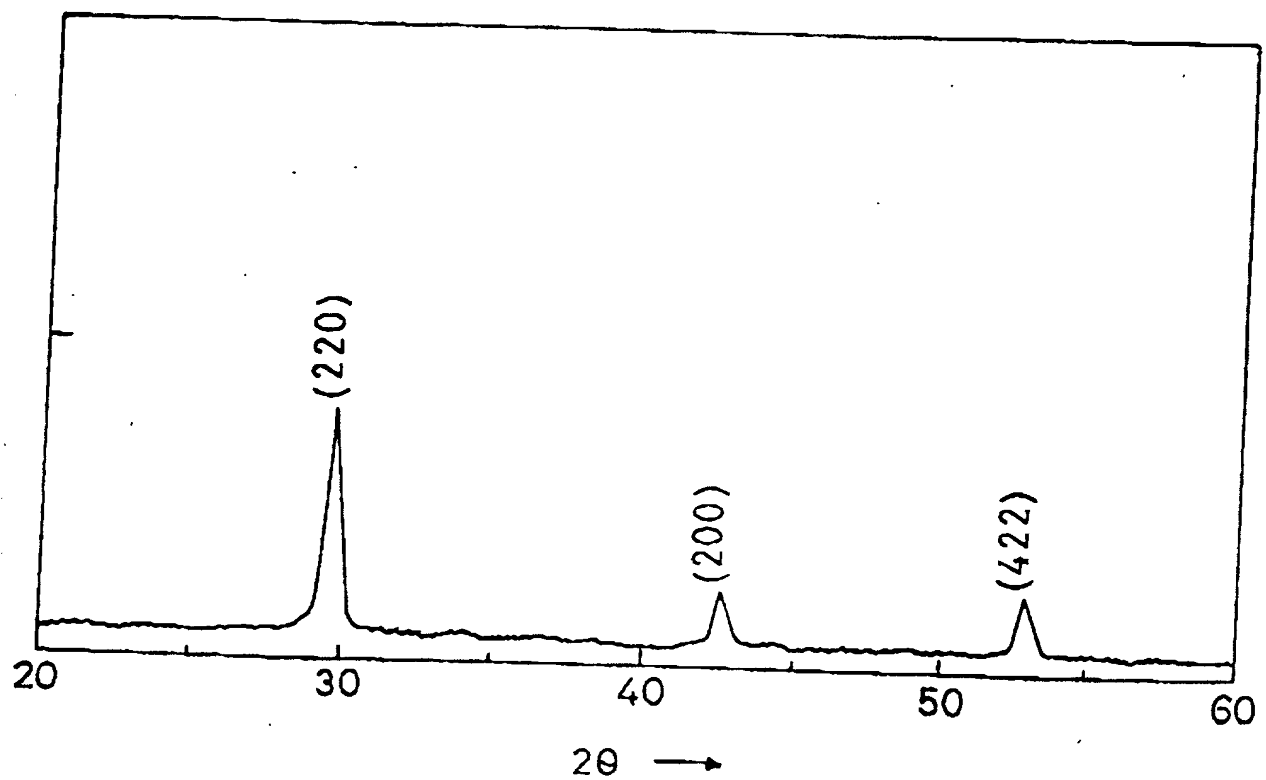


Fig 6(a)

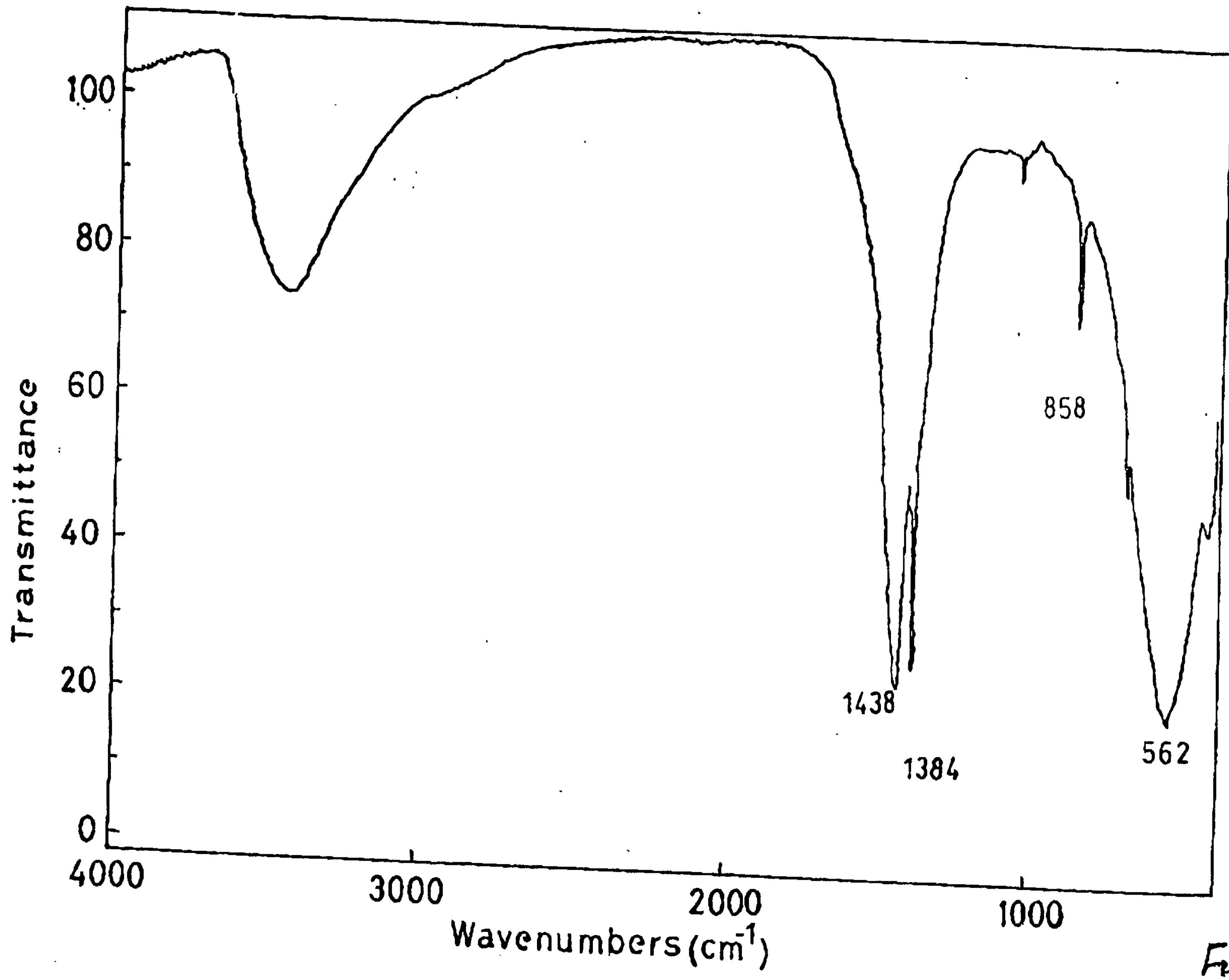

Transmittance
100
80
60
40
20
0
4000
3000
2000
1000
Wavenumbers (cm⁻¹)
1438
1384
858
562

Fig 6(b)

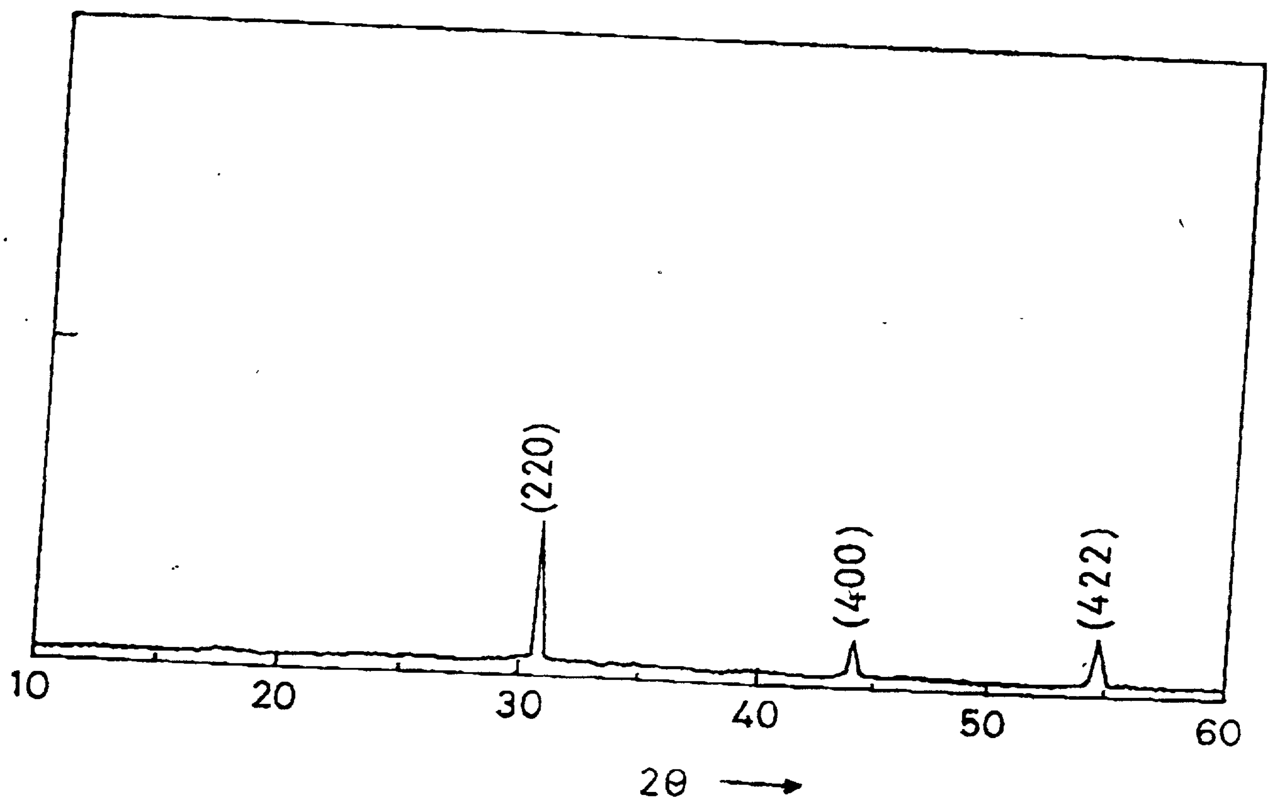


Fig 7(a)

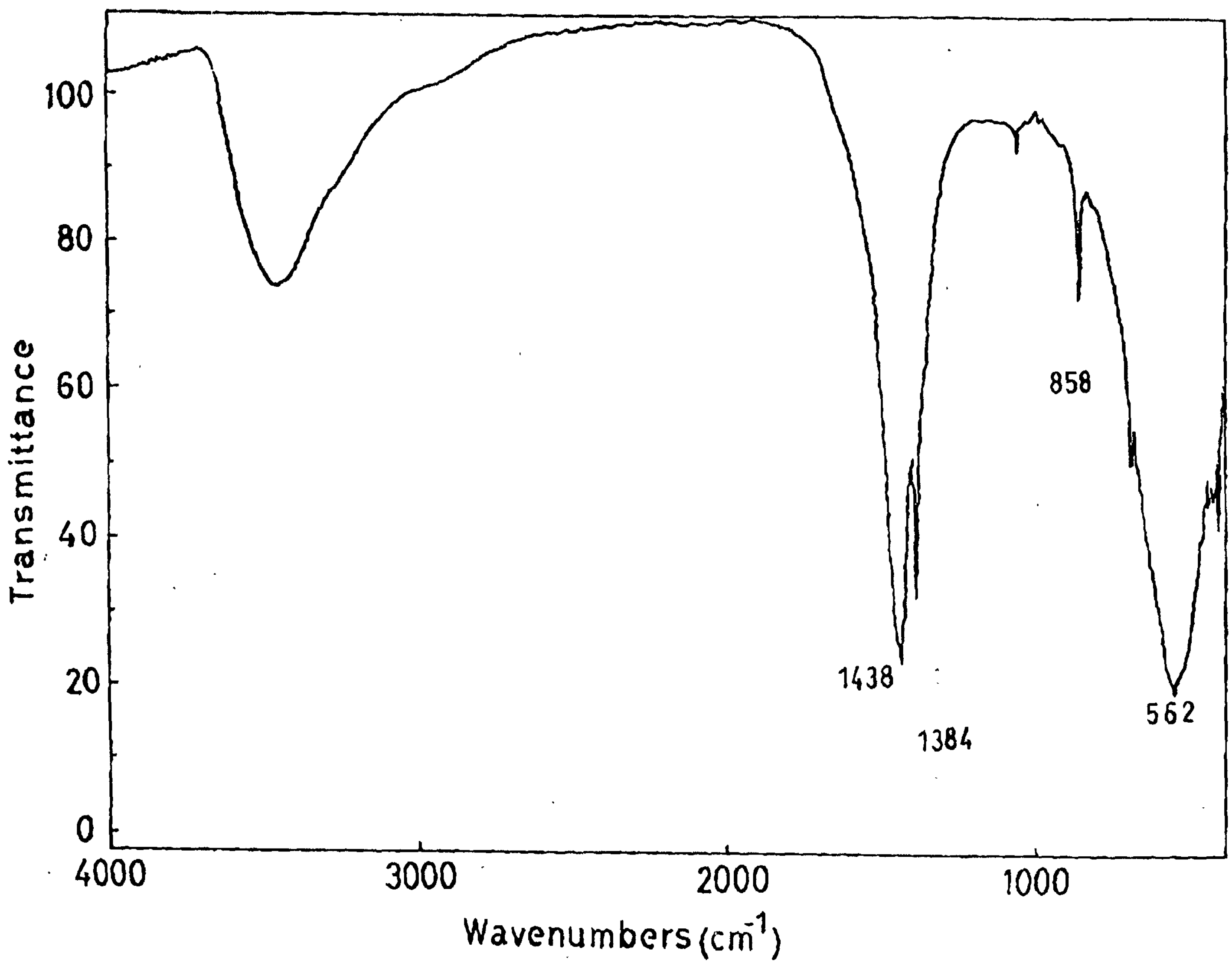

Transmittance
100
80
60
40
20
0
4000
3000
2000
1000
Wavenumbers (cm^{-1})
1438
1384
858
562

Fig 7(b)